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1,8 - Dinitronaphthalene as a Cathode Material in a Magnesium/ Zinc Based Primary Battery

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The efficiency of 1-8 dinitronaphthalene as a cathode material in a magnesium/zinc based primary battery is examined. The discharge performance of the cell is investigated under different parametric variations such as pH, temperature, nature of electrolyte, current drain, and zeolite modification. Depending on the current drain and pH of the electrolyte, 8e or 10e reduction takes place.

Introduction

Organonitro compounds have received considerable attention as battery cathodes[1-11]. Recent developments in the field include development of novel polynitro organic cathodes, to pack more energy into the battery. In a polynitro compound the position of the nitro groups is a critical factor that derermines its coulombic efficiency. Each nitro group exerts perfound influence on the extent of reduction of the other nitro groups. In such situations the reduction of the other nitro groups may go to completion or may remain at partially reduced states. Inter-and intra-molecular condensation of reduction products amongst themselves or with the reactant(s) is another problem that impedes the efficiency of the nitro compound based cathodes. Therefore, various nitro compounds have been examined in the laboratory by the authors for battery application[7-11]. Here, the battery discharge performance of 1-8-dinitronaphthalene is discussed.

Experimental Procedure

Unless otherwise specified, all chemicals used were E Merck extrapure products. 1-8-dinitronaphthalene was prepared by following Hodgson and Walkers' procedure[12]. The details of cell construction, cell discharge, zeolite modification, IR spectral analysis and electrochemical characterization are described earlier[13]. The Raman spectral procedure is reported earlier[14]. Double distilled water was used in preparing the electrolyte solutions. The zeolite used was a β -zeolite (Union Catalysts, India).

Results and Discussion

General Discharge Performance

The discharge performance of 1-8-dinitronaphthalene in magnesium and zinc based cells revealed that neither high nor low compaction pressure was suitable for the performance of the cells. An optimum compaction pressure of 340 kg/cim^2 applied over the cathode area and 80 wt per cent colloidal graphite (Figure 1) were adequate for good performance in both Zn and Mg based cells. In magnesium cells, magnesium choloride was superior to magnesium perchlorate and bromide. A small amount of V_2O_5 (0.1 wt per cent) increased to Ah capacity by about 7 per cent. Zeolite modification[15-18] effected a remarkable increase in the Ah capacity (Figure 2). With decrease in temperature, there was a progressive decrease in the discharge capacity of the zinc based cells together with a slight decrease

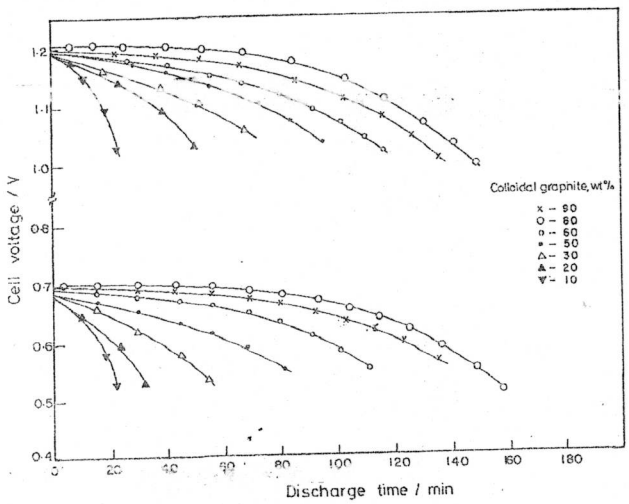


Figure 1 — Effect of colloidal graphite content on the discharge performance of $Mg/MgCl_2$-1,8-dinitronaphthalene. (0.185 g) cell. Compaction pressure: 340/kg.cm3 ; constant current drain=50 mA

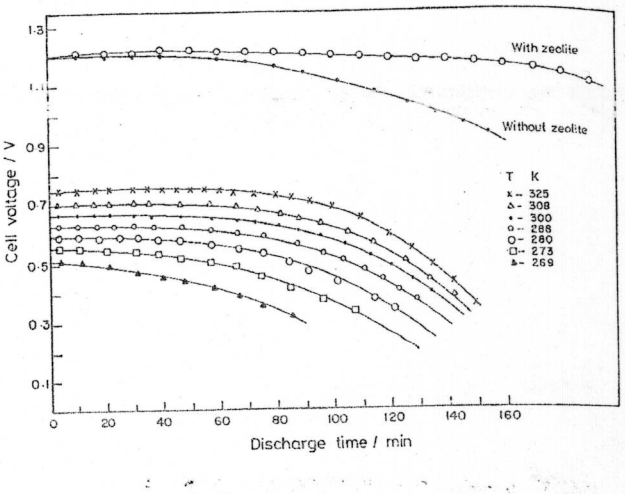


Figure 2 — Effect of temperature variation on discharve performance of zinc-1,8-dinitronaphthalene. (0.185g) cell. The effect of zeolite modification on a $Mg/MgCl_2$ cell is also shown

Table 1 — Ah capacity of 108-dinitronaphthalene cathode under different test conditions current collector: copper mesh, Battery plate size $(4\times2.5)10^4$ m2

Anode	Electrolyte	V_2O_5 catalyst	Current drain, mA	Zeolite modification	Capacity/Ah/g
Mg	2 M $MgCl^2$	—	10	—	1.04
Mg	2 M $MgCl^2$	0.1 wt. per cent	10	—	1.10
Zn	$ZnCl_2/NH^4Cl$	—	10	—	1.08
Zn	$ZnCl_2/NH^4Cl$	—	30	—	0.95
Zn	$ZnCl_2/NH^4Cl$	—	50	—	0.66
Zn	$ZnCl_2/NH^4Cl$	0.1 wt. Per cent	10	Yes	1.21
Zn	1,5 M H_2SO_4		10	—	1.30
Zn	Walpole acetate buffer pH 5.6	—	10	-	0.76

in cell voltage. However, as expected, magnesium cells exhibited good low temperature performance.

Effect of pH and Current Drain

In acidic electrolyte (1.5 M H_2SO_4) with zinc as the anode, the Ah capacity is the highest; with $ZnCl_2/NH_4Cl$ electrolyte the Ah capacity was less and in the Walpole acelate buffer (pH 5.6) as the electrolyte the Ah capacity was still less (Table 1). Further, in the $ZnCl_2/NH_4Cl$ electrolyte, current drain has a profound influence. At low current drain (5-10 mA) the coulombic efficiency is the highest, followed by medium current drain (30-50 mA) and high current drain($\geq$ 75 mA) (Table 1).

Spectral Analysis

The IR spectra of the organic compounds isolated from the end-of-discharge products with copper mesh as the current collector, Zn as anode and $ZnCl_2/NH_4Cl$ as the electrolyte are shown in Figure 3. As is evident the spectra of the products are completely diffferent from that of 1-8-dinitronaphthalene (Figure 3, curve a). It can be seen that the absorptions characteristic of the nitro group (1550, 1420 and 880/

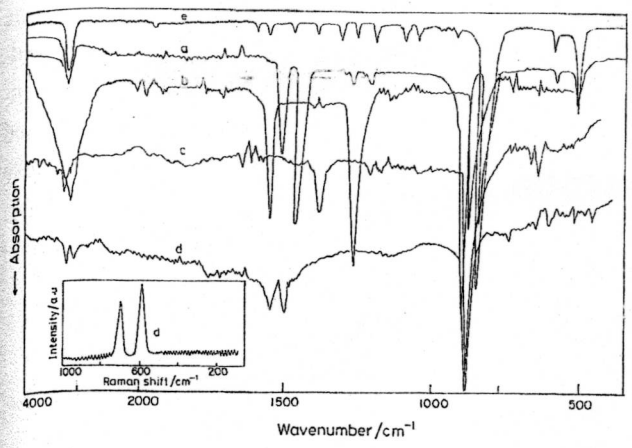


Figure 3 — IR spectrum of : (a) 1,8-dinitronaphthalene and end-of-discharge product, (b) low current drain, 10 mA, (c) medium current drain, 50 mA, (d) high current drain, 100 mA. Curve e is the IR spectrum of naphgthalene

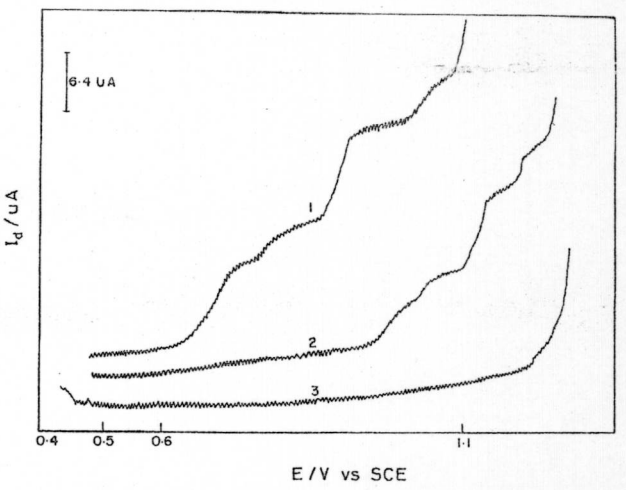


Figure 4 — dc polarogram for the end-of-discharve product from a $Zn/ZnCl_2$-NH_4Cl/1,8-dinitronaphthalene cell discharge at (1) 50 mA, (2) 10 mA, and (3) 100 mA

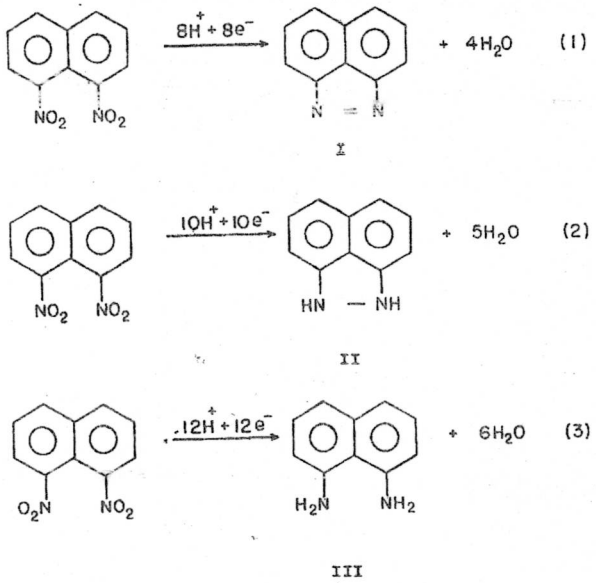
Table 2 — Yield of products from a $Zn/ZnCl_2$ - NH_4Cl based cell, cathode plate size $(4\times2.5)10^{-4}m2$

Current drain, mA	Product	Yield, per cent
10		77
50		79
100		72

cm) (ref.19) are absent in the spectrum of the products. On the other hand, frequencies characteristic of NH_2 functionality at 3380, 1580 and 1250/cm are seen in Figure 3 curve b (low current drain, 10 mA product) Figure 3, curve c (50 mA discharge) exhibits a single medium intensity absorption at 1400/cm which could be attributed to the HN-NH bonding. Curve d in Figure 3 is the IR spectrum of the high current drain product (100 mA discharge). It exhibits onspicuous absorptions at 1420/cm which could be attributed to N=N frequency[20]. The N=N frequency is generally weak and is not generally clearly exhibited in the IR spectrum. On the other hand the Raman spectrum (Figure 3, inset) presents the absorption distinctly[21]. Curve e in Figure 3 is the IR spectrum of napthalene which shows a strpmg anspr[topm at 975/cm. This absorption is retained in curves b and d; however, some shift is observed in curves a and c. This observation indicates the influence of the bridging N=N bond on the structure of the napthalene ring. The dc polarograms for the products corresponding to curves b, c and d in the IR spectra are shown, respectively, in curves 3, 1 and 2 in Figure 4. The absence of reduction process in Figure 4, curve 3 supports that it is a diamino compound. The reduction modes of - NH-NH and - N=N- bonding are exhibited, respectively in curves 2 and 1 of Figure 4.

Mechanism of Cell Discharge

By careful working up of the end-of-discharve products and separation by column chromatography the yield of each of the products has been quantified. The values are presented in Table 2. Based on the Ah capacity the yields of products, comparison with authentic samples by NMR and mass spectros-



Scheme I

copy[22] and in the light of the spectral data, the following mechanism (Scheme 1) is proposed for the electrochemical reactions responsible for the battery discharge. Lo Presti *et al*[23] who have made polarographic and coulometric studies of dinitronaphthalene have proposed similar mechanism for the electroreduction of 1-8-dinitronaphthalene.

In 1.5 M H_2SO_4 with Zn anode, a single 12e reaction takes place with 93 per cent conversion at a cut off voltage of 0.5. In $Zn/ZnCl_2$-NH_4Cl electrolyte, depending on the current drain in 12e (77 per cent conversion) or a 10e (79 per cent conversion) or a 8e (72 per cent conversion) takes place. However, in each case, there was only one product viz. respectively III (12e), II (10e) and the I (8e), compounds as shown in Scheme 1.

Conclusions

1-8-Dinitronaphthalene is found to be an active material for battery cathodes. Depending on the pH and current drain, the reaction goes through 8e or 10e or 12e reaction. The end-of-discharge products are brightly coloured compounds from red orange (8e) to red-brown (10e) to brown (12e). These products are of practical importance as dyes or dye intermediates. The fact that these products are formed exclusively without side reactions during battery discharge indicates a pathway of using battery as a tool to tap energy at the same time harvesting novel compounds of practical importance.

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